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Fe^{2+} and Fe^{3+} oxidation states on natural sapphires probed by X-ray absorption spectroscopy

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Abstract

Sapphire is the inorganic gemstone in varieties of gem corundum with the pure alpha-alumina (α-Al_2O_3) structure showing colorless. The various colors of sapphire are caused by some trace elements such as Cr, Fe, and Ti. Natural sapphires occur in different geological origins such as basaltic and metamorphic host rocks. High-quality sapphires contain low inclusion. The sapphire qualities are based on their sources that are hardly identified by the gemological instrument. In this study, X-ray absorption spectroscopy (XAS) focused on X-ray absorption near edge structure (XANES) technique using the Synchrotron radiation is employed for identifying the origins of sapphire samples. In particular, Fe *K*-edge XANES spectra are applied to analyze the Fe oxidation states on sapphires. As the results, we conclude that there were the Fe^{2+} from some mineral inclusions and Fe^{3+} which substitute Al^{3+} on the sapphire structure from both basaltic and metamorphic sources.

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Keywords: sapphire; x-ray absorption spectroscopy; iron oxidation states; synchrotron radiation

1. Introduction

Natural alpha-alumina (α-Al_2O_3) known as corundum applied for gem materials such as ruby and sapphires[1]. Pure corundum is colorless, however, the other color of corundum caused by the vacancies of trace elements as the

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structural defect[2,3]. For example; Cr^{3+}, Fe-Ti pairs, and Fe^{3+} produced red, blue and yellow, respectively. Corundum crystals with colors except red are called sapphires. Sapphires have been originated in various geological origins that are related to either basaltic or metamorphic sources[4]. Nowadays, the identification of sapphire sources is based on the experiences of gemologists. The color hue of sapphires is one of the factors to classify their sources and their qualities[1]. The defect properties such as dielectric constant were applied to study the causes of color in sapphires[5]. Initially, the Fe atoms in sapphire structure play an important role to produce the different coloration[2]. However, there were two Fe oxidation states such as Fe^{2+} and Fe^{3+} proposed to create the color of sapphires probed by UV-Vis spectroscopy and electron spin resonance (ESR)[2,3,6]. Therefore, the Fe oxidation states on natural sapphire structures could be analyzed for better understanding the coloration of sapphire.

In this study, the Fe oxidation states on natural sapphires collected from different origins will be measured by X-ray absorption spectroscopy (XAS) using the Synchrotron radiation.

2. Materials and Methods

2.1. Sample preparation

The natural sapphire samples were collected from various geological origins, i.e., basaltic and metamorphic ones as shown in Figure 1. For basaltic sapphires, the samples were selected from Thailand whereas the metamorphic ones were selected from Sri Lanka gem fields. The samples were polished in gem-trade level and found the c axis by polariscope to precisely record the direction of X-ray beam for XAS measurement, such as parallel and perpendicular to the c axis. Moreover, there were the Fe-oxide standards in powder form for referring the oxidation states including Fe foil (as Fe^0) FeO (as Fe^{2+}), Fe_2O_3 (as Fe^{3+}) and Fe_3O_4 (as $Fe^{2+,3+}$).

(a) Basaltic sapphires (b) Metamorphic sapphires

Fig. 1. The natural sapphire samples in this study

2.2. X-ray absorption spectroscopy

XAS measurement of the natural sapphire samples focused on Fe *K*-edge using XANES technique in fluorescence mode. The Fe *K*-edge XANES spectra were measured at XAS Beamline-8 station, located in the Synchrotron Light Research Institute (SLRI), Thailand, employing the synchrotron radiation beam from eight bending magnets[7]. The XAS technique is suitable for gemstone because of the non-destructive method[8]. In this study, the XANES measurement was set to detect the spectra at Fe *K*-edge, which calibrated at 7112 eV referred to the binding energy (E_0) of Fe^0 oxidation states. The Ge (220) double crystal monochromator was used with 0.1 meV to 0.3 meV energy resolution depended on the width of entrance slit. The specific parameters of this measurement for the sapphire samples were -20 eV to +120 eV with 0.2 eV energy step width and 5 s derivative time using the 13-channel array germanium detector to obtain the spectra for four times scan.

Principally, the absorption coefficient of the sapphire samples measured in fluorescence mode could be calculated by the Eq. 1[9].

$$I_f / I_0 = \mu x \quad (1)$$

Besides, the Fe *K*-edge XANES spectra of Fe-oxide standards were carried out using the transmission mode. The absorption coefficient was calculated by the Eq. 2[9].

$$\ln (I_0 / I) = \mu x \quad (2)$$

Where; μ is the absorption coefficient, I_0 is the intensity of incident X-ray, I_f is the intensity of fluorescent X-ray, I is the intensity of transmitted X-ray and x is the thickness of the sample.

2.3. Data analysis

The Fe *K*-edge XANES spectra were analyzed using Athena software.

3. Results and Discussion

The Fe *K*-edge XANES spectra of Fe-oxide standards (Figure 2 and Table 1) indicate that the Fe oxidation states are classified by the rising edge position referred to the binding energy (E_0) as well as the pre-edge features. Figure 3 shows the Fe *K*-edge XANES spectra of natural sapphires from the representative basaltic origin compared to the metamorphic one. The rising edge position of both sources is detected at 7124 eV corresponding to the position of the Fe_3O_4 standard. Hence, the mixture of Fe^{2+} and Fe^{3+} oxidation states on sapphires evidencing to the edge position could be proposed. The Fe^{2+} derived from some nano mineral inclusions such as ilmenite ($FeTiO_3$) detected by transmission electron microscopy[10] while Fe^{3+} that substitute Al^{3+} detected from the sapphire host. The photon energy positions of Fe *K*-edge XANES spectra on sapphire samples are also shown in Table 1.

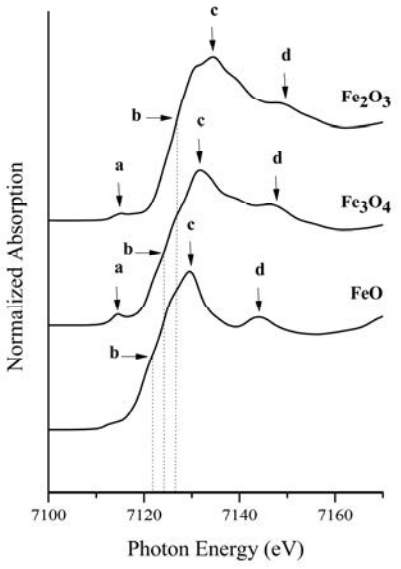

Fig. 2. The Fe *K*-edge XANES spectra of Fe-oxide standards

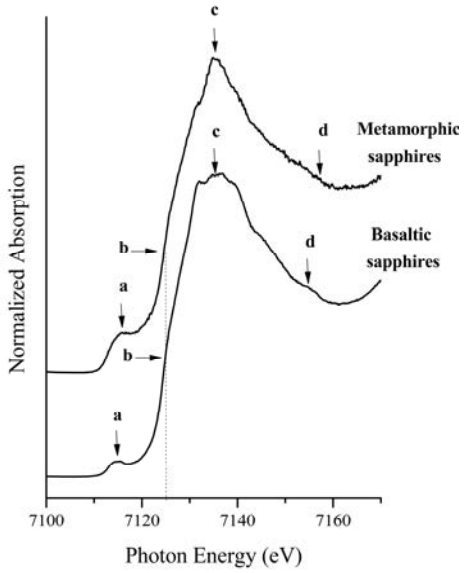

Fig. 3. The Fe *K*-edge XANES spectra of natural sapphires

Table 1. The photon energy positions of Fe *K*-edge XANES spectra on Fe-oxide standards and natural sapphires

Sample	Oxidation state	Pre-edge position; a (*eV*)	Rising edge position; b (*eV*)	Edge jump position; c (*eV*)	Post-edge position; d (*eV*)
FeO	Fe^{2+}	none	7122	7130	7144
Fe_3O_4	Fe^{2+} and Fe^{3+}	7114	7124	7132	7147
Fe_2O_3	Fe^{3+}	7116	7126	7134	7149
Basaltic sapphires	Fe^{2+} and Fe^{3+}	7114	7124	7132	7154
Metamorphic sapphires	Fe^{2+} and Fe^{3+}	7115	7124	7134	7157

4. Summary

Fe *K*-edge XANES spectra of natural sapphires can be obtained from XAS experiment. From the spectra, it is possible to specify the Fe oxidation states on sapphire samples. The Fe^{2+} and Fe^{3+} oxidation states are detected in the sapphires from both basaltic and metamorphic sources compared to those of the Fe-oxide standards. It could be indicated that Fe^{2+} located at some nano mineral inclusions (i.e., ilmenite; $FeTiO_3$) and Fe^{3+} substituted Al^{3+} at the sapphire host.

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